Property of Opal as Photonic Crystal Electrochemically Infiltrated with Polythiophene and Polypyrrole

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Abstract

Three-dimensional periodic structures of the porous synthetic opals as photonic crystals have been infiltrated with polypyrrole and polythiophene by electrochemical polymerization.

Drastic shifts of the peak in the reflection spectrum and the sharp dip in the transmission spectrum have been observed upon infiltration.

Tunability of the reflection peak has been demonstrated in the opals infiltrated with conducting polymer upon electrochemical doping and undoping.

KEYWORDS： opal, photonic crystal, conducting polymer, polypyrrole, polythiophene, electrochemical polymerization, reflection, stop band

ポリチオフェン及びポリピロールを電気化学的に浸透させたフォトニック結晶としてのオパールの性質

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３次元周期構造を持ったフォトニック結晶としての多孔性人工オパールに電気化学重合法により、ポリチオフェン及びポリピロールを浸透させた。浸透により反射スペクトルのピーク及び透過スペクトルの落ち込み位置は大きく動いた。また導電性高分子浸透オパールにおいて電気化学的ドープ、脱ドープにより反射ピークのチューナビリティを実現した。

1. Introduction

Since the theoretical prediction of a new concept of photonic crystal with a photonic band gap in which some energy range of photons are forbidden to exist, the photonic crystal with a three-dimensional periodic structure of the optical wavelength order has attracted much interest from both fundamental scientific and practical industrial view points[1-3].

Among various methods of preparation of three-dimensional periodic structure, we have utilized the most simple method of the sedimentation of SiO_2 spheres of several hundreds nm in diameter dispersed in water. The prepared three-dimensional periodic structure of SiO_2 can also be named as a synthetic opal.

We have demonstrated that various materials can be infiltrated into the interconnected periodic array of nano-scale voids in the synthetic opal[4]. We also proposed a tunable photonic crystal in which the photonic band gap can be tuned by controlling the periodicity, fraction and refractive index etc, by external fields or ambient condition[5]. Indeed we exhibited the control of the reflection peak and the transmission dip in synthetic opals as photonic crystals infiltrated with various materials[6-8].

In this paper, the three-dimensional periodic array of voids in the synthetic opals and the opal replicas are successfully infiltrated with conducting polymers by electrochemical polymerization. Utilizing conducting polymer infiltrated opals the control of the transmission and reflection spectra are also demonstrated.

2. Experimental

Three-dimensional periodic structure of the synthetic opals with thickness of about several ?m were prepared on indium-tin-oxide (ITO)-coated glass plates by the sedimentation of mono-dispersed SiO_2 spheres of several hundreds nm in diameter.

Polymer replicas of these opals were also prepared upon introduction of photopolymers in the nano-scale voids of the SiO_2 opals and subsequent removal of silica by washing with hydrofluoric acid (HF).

The structures of the obtained opal film and polymer replica were observed using a scanning electron microscope (SEM) (S-2100A, Hitachi). The transmission spectra were measured using a HP8452A spectrophotometer and the reflection spectra at normal incidence were measured using a W-lamp light as the light source and a PMA-11 (Hamamatsu photonics) as a detector.

The opal film on ITO plate as a working electrode, a counter electrode (Pt) and a reference electrode (Ag) were immersed in the electrolyte solution of $LiBF_4$/benzonitrile and $LiBF_4$/distilled water containing thiophene and pyrrole monomers, respectively.

Upon application of voltage to the working electrode with positive polarity, conducting polymers were electrochemically polymerized in the nanoscale voids.

3. Results and Discussion

The obtained opal films and photopolymer replicas exhibit beautiful opalescent colors and clear diffraction peaks depending on the periodicity and the effective refractive index.

Figure 1 shows reflection spectra in air and the SEM images of the synthetic opal film fabricated with SiO_2 spheres of 300 nm in diameter and photopolymer replica. This opal film has a regular array of SiO_2 spheres, as can be seen from this image. It is also confirmed that the periodicity evaluated from the reflection peak coincides with the SEM image.

Photopolymer replica has an inverted structure of this synthetic opal, as is also shown in the inset of Fig. 1. The obtained replica consists of the photopolymer template and air spheres instead of

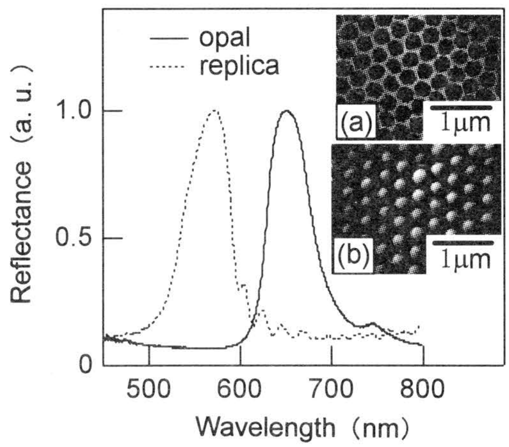

Fig.1 : The reflection spectra of synthetic opal fabricated from SiO_2 spheres of 300 nm in diameter and photopolymer replica. The inset shows SEM images: (a) photopolymer replica. (b) synthetic opal.
図1　直径300nmのSiO_2球を用いて作製された人工オパールとフォトポリマーレプリカの反射スペクトルと走査電子顕微鏡写真 (a) フォトポリマーレプリカ (b) 人工オパール

the removed SiO_2 spheres. In addition it should be noted that air spheres are connected at the contact points of SiO_2 spheres in the original opal. That is, it is also possible to infiltrate various materials into a replica. It should be also mentioned that the volume of voids in the replica is much larger than that in the opal.

Electrochemical polymerization of polypyrrole and polythiophene in the voids was carried out by applying 1 V for about 6 hours and 3 V for about 1 hour, respectively. The infiltrated conducting polymers are in the doped state.

Figures 2 and 3 indicate reflection spectra of both the synthetic opal and the synthetic opal infiltrated with polypyrrole in air, and those of both the photopolymer replica and the the photopolymer replica infiltrated with polythiophene in air, respectively. As evident in these figures, clear peak whose wavelength depends on volume fractions of the opal and the composition was observed in the reflection spectra. It should be noted that the reflection peak shifted drastically to longer wavelength upon infiltration of polypyrrole and polythiophene into the interconnected nano-scale regular array of voids of the synthetic opal and photopolymer replica by electrochemical polymerization. The dip in the transmission spectra was also confirmed to shift drastically upon infiltration of the voids with conducting polymer by the electrochemical polymerization.

The refractive index of the infiltrated conducting polymer is evaluated from the reflection peak. That is, the periodicity of the synthetic opal and the phtopolymer replica is evaluated from the reflection peak in air before infiltrating conducting polymer. Then, utilizing thus evaluated periodicity and the peak wavelength, the refractive index of the infiltrated conducting polymer was estimated. From the shift of the peak wavelength, by assuming full infiltration, the refractive indices of polypyrrole and polythiophene in the doped state were evaluated to be about 1.45 and 1.42, respectively. The evaluated refractive indices were confirmed to be in the range of the values measured by other method so far reported[9-11]. Though, whether the infiltration is complete or not, is uncertain at this stage, these facts clearly support that the interconnected nano-scale voids of the synthetic opals and photopolymer replicas are infiltrated with conducting polymers. It was also confirmed

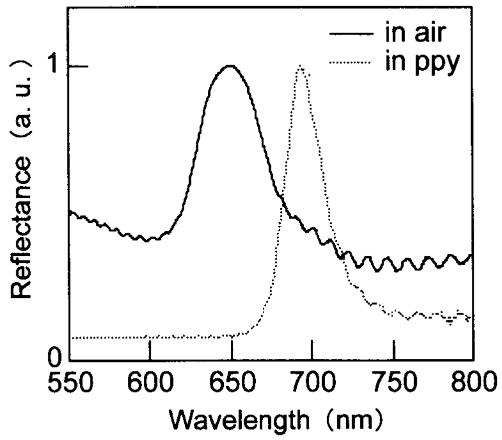

Fig.2 : The reflection spectrum of synthetic opal fabricated from SiO2 spheres of 300 nm in diameter in air and that of polypyrrole infiltrated opal.
図2　直径300nm の SiO2球を用いて作製された人工オパールの電気化学的重合法によるポリピロール浸透前後の反射スペクトル

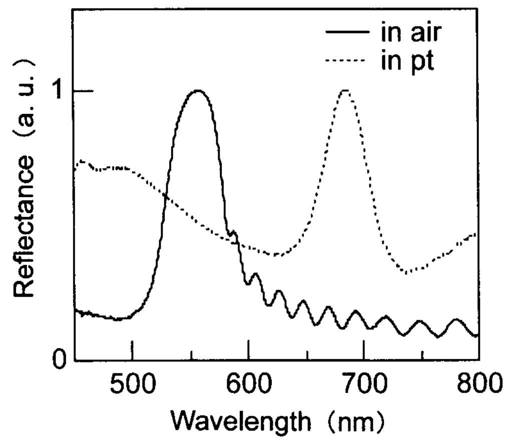

Fig.3 : The reflection spectrum of photopolymer replica in air and that of polythiophene infiltrated photopolymer replica.
図3　フォトポリマーレプリカの電気化学的重合法によるポリチオフェン浸透前後の反射スペクトル

that anions in the electrolyte were electrochemically doped in the conducting polymer in the nano-scale.

Figure 4 indicates the change of the reflection spectra of the photopolymer replica infiltrated with polythiophene with application of the constant voltage as a function of time. As evident in this figure, with increasing doping level, the peak wavelength of the reflectance spectra changed drastically to a shorter wavelength. It should be also noted that these shifts of the reflection spectra were confirmed to be reversible by controlling the applied voltage. That is, by this procedure we can realize the control of the reflection peak by the electrochemical doping into the conducting polymer infiltrated into the photopolymer replica matrix.

The doping time dependence of the peak wavelength of reflection spectra in the polythiophene infiltrated photopolymer replica upon electrochemical doping is shown in Fig. 5. The shift of reflection peak with increasing doping level is attributed to the decrease of the refractive index of polythiophene.

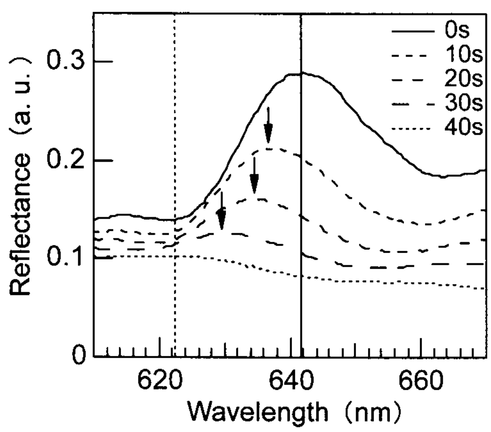

Fig.4 : Change of reflection spectra of the photopolymer replica infiltrated with polythiophene with constant voltage as a function of time.
図4　一定電圧下でのドーピング変化によるポリチオフェン浸透フォトポリマーレプリカの反射スペクトルの時間依存性

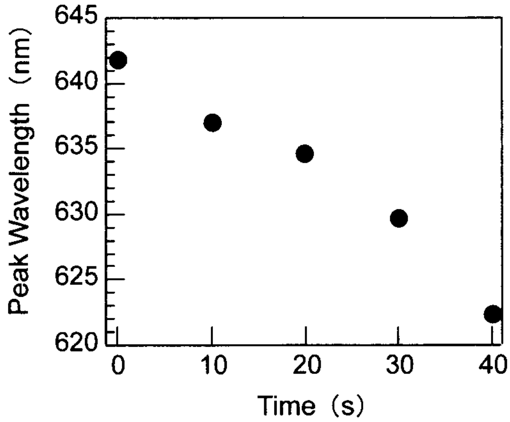

Fig.5 : Doping time dependence of the peak wavelength in the reflection spectra of photopolymer replica infiltrated with polythiophene.
図5　ポリチオフェン浸透フォトポリマーレプリカの反射スペクトルのピーク波長のドーピング時間依存性

4. Summary

The results of this experimental study can be summarized as follows. The optical properties of the synthetic opal and the opal replica with a three-dimensional periodic structure, such as transmission and reflection spectra, were found to change drastically upon infiltration with conducting polymer by electrochemical polymerization. In the synthetic opal and the replica infiltrated with conducting polymer, the control of the reflection peak was demonstrated by the electrochemical doping and undoping.

These results indicate that the tunability of the optical properties in the synthetic opal infiltrated with conducting polymer can be realized.

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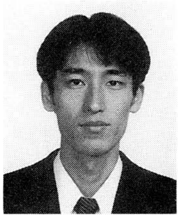

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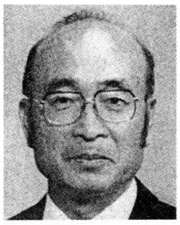

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